

Mapping the dynamics of complex multi-dimensional systems onto a discrete set of states conserving mean first passage times: a Projective Dynamics approach

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Abstract

We consider any dynamical system that starts from a given ensemble of configurations and evolves in time until the system reaches a certain fixed stopping criterion, with the mean first-passage time the quantity of interest. We present a general method, Projective Dynamics, which maps the multi-dimensional dynamics of the system onto an arbitrary discrete set of states $\{\zeta_k\}$, subject only to the constraint that the dynamics is restricted to transitions not further than the neighboring states $\zeta_{k\pm 1}$. We prove that with this imposed condition there exists a master equation with nearest-neighbor coupling with the same mean first-passage time as the original dynamical system. We show applications of the method for Brownian motion of particles in one and two dimensional potential energy landscapes and the folding process of small bio-polymers. We compare results for the mean first passage time and the mean folding time obtained with the Projective Dynamics method with those obtained by a direct measurement, and where possible with a semi-analytical solution.

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INTRODUCTION

The mean first-passage time (MFPT) is the time required for an ensemble of identical systems starting from a given initial distribution of configurations to reach a fixed criterion. Being able to obtain the MFPT is important in a wide array of physical applications. These include the MFPT when a star of a certain mass goes supernova, to neuron firing dynamics, spreading of diseases, chemical kinetics, folding processes of polymers, the death of living creatures, and the decay of metastable states via nucleation and growth processes [1, 2]. The Projective Dynamics (PD) method to calculate MFPT for systems with a discrete state space [3–6] mapped the MFPT problem for metastable decay of magnetic states associated with Ising-type (discrete spin states) models onto a nearest-neighbor coupled master equation. However, the PD method has not previously been shown to be valid for other dynamical systems, for example for systems with continuous state spaces [7]. The calculation of the MFPT for systems with long time scales has previously required that the dynamic system satisfy certain conditions. For example, for the milestoning method [8] to work the system must be close to equilibrium or have separation of time scales or committer surfaces. We prove in this letter that the PD method has no such constraints, and hence it is generally applicable to obtain the MFPT of *any* dynamical system.

We prove that for any MFPT problem (with a finite MFPT) there exists a discrete master equation with nearest-neighbor coupling that has the same MFPT as the original system. This master equation has time-independent rates, even if the underlying system is non-Markovian. Every point in phase space in the original system must be mapped onto a state in the discrete master equation. We show that *any* mapping that leads to only nearest-neighbor coupling in the master equation preserves the MFPT provided the growing (g_k) and shrinking (s_k) rates between all master equation states k are correct. Therefore, whether the g_k and s_k are known theoretically or are measured, the correct MFPT is obtained. For metastable decay in the ferromagnetic $d=3$ Ising case such knowledge enabled calculations of MFPT of about 10^{50} Monte Carlo steps per spin [5]. It is anticipated that the knowledge that the PD method gives the correct MFPT will enable long-time-scale simulations for other physical models. An example of where the PD method may be useful for long-time simulations is studies of the intercalation time of Li ions in molecular dynamics studies modeling charging of batteries [9].

THEORY

Consider any ensemble of systems evolving in phase space Γ under some dynamic. They start with some given distribution, and we desire to calculate the MFPT until each system stops after it meets some fixed stopping criterion. The dynamics of the ensemble can be mapped onto a set of discrete non-overlapping states $\{\zeta_k\}$, with $0 \leq k \leq S$, which cover the entire domain. We impose the restriction that the states ζ_k can make transitions only to the states $\zeta_{k \pm 1}$. This condition can be met for many systems by adjusting the ‘length’ $\Delta\zeta$ of the states, so that no transitions within a single time step dt further than to the neighboring states exist. The states that form the stopping criterion will all be mapped to ζ_0 .

The time-evolution of the system can be described by a master equation with nearest neighbor coupling, which describes the change of occupation $P_k(t)$ of state k by the probability flows between adjacent states. Namely,

$$\frac{d}{dt}P_k(t) = g_{k+1}P_{k+1}(t) - [g_k + s_k]P_k(t) + s_{k-1}P_{k-1}(t), \quad (1)$$

where the growing g_k (shrinking s_k) rates represent the directional rates at which the system transits from state k to state $k - 1$ ($k + 1$). The initial conditions $\{P_k(0)\}$ are specified by the ensemble of initial conditions of the original system.

Let $N(k \rightarrow k \pm 1; t, t + dt)$ denote the number of times the system makes a transition from state k to its neighboring states ($k \pm 1$) in the time interval $(t, t + dt]$ and $N_k(t)$ the number of times the system resides in state k at time t . Then the growing rate for the time interval $(t_o, t_e]$ can be obtained by measuring the system at time intervals dt . Explicitly

$$g_k dt = \frac{\int_{t_o}^{t_e} dt N(k \rightarrow k - 1; t, t + dt)}{\int_{t_o}^{t_e} dt N_k(t)}. \quad (2)$$

A similar expression exists for the shrinking rate s_k .

Assuming that the ensemble of systems has been fully absorbed at $t_e = \infty$ after starting at $t_o = 0$, we write in shorthand the master equation

$$\frac{d}{dt}P_k(t) = \sum_{k'} W(k, k') P_{k'}(t), \quad (3)$$

where the elements of $W(k, k')$ are the growing and shrinking rates, which have been measured from $t_o = 0$ up to some point in time when all systems in the ensemble are fully

absorbed. By using the fundamental relation [10] $\sum_k \tau(k)W(k, k') = -1$, the general expression for the MFPT $\tau(S_o)$ for a system starting fully in state S_o can be obtained as

$$\tau(S_o) = \sum_{i=1}^{S_o} \frac{1}{g_i} + \sum_{\ell=1}^{S-1} \left[\sum_{i=1}^{\min(S_o, |S-\ell|)} \left(\frac{\prod_{j=i}^{i+\ell-1} s_j}{\prod_{j=i}^{i+\ell} g_j} \right) \right] \quad (4)$$

where S_o denotes the starting state and S the total number of states within the domain.

We prove that Eq. (4) gives the same MFPT independent of the particular choice of the states. For this purpose, let $m \equiv k \cup k+1$ be the joined interval of state k and $k+1$, then for a single time step it follows that the transitions from state m to $k-1$ ($k+2$) in the new system are equal to the transitions from state k to $k-1$ ($k+1$ to $k+2$) in the old system namely $\tilde{N}(m \rightarrow k-1, t, t+dt) = N(k \rightarrow k-1, t, t+dt)$ and $\tilde{N}(m \rightarrow k+2, t, t+dt) = N(k+1 \rightarrow k+2, t, t+dt)$, whereas the probability of occupation of state m rescales as $\tilde{P}_m(t) = P_k(t) + P_{k+1}(t) = [N_k(t) + N_{k+1}(t)] / \sum_k N_k(t)$. Thus the growing rate at time t in the old and new system are related as

$$\tilde{g}_m = \frac{P_k(t)}{P_k(t) + P_{k+1}(t)} g_k \quad (5)$$

and similarly for the new shrinking rate \tilde{s}_m .

That this procedure leaves the MFPT unchanged can be understood by noting the effect of joining two states on the master equation. The joining of adjacent states corresponds to the addition of terms of the master equation of the same adjacent states, namely

$$\frac{d}{dt} P_k(t) = g_{k+1} P_{k+1}(t) - [g_k + s_k] P_k(t) + s_{k-1} P_{k-1}(t). \quad (6)$$

and

$$\frac{d}{dt} P_{k+1}(t) = g_{k+2} P_{k+2}(t) - [g_{k+1} + s_{k+1}] P_{k+1}(t) + s_k P_k(t). \quad (7)$$

It is easily seen that the cross terms vanish and we are left with an expression of the form

$$\frac{d}{dt} \tilde{P}_m(t) = g_{k+2} P_{k+2}(t) - g_k P_k(t) - s_{k+1} P_{k+1}(t) + s_{k-1} P_{k-1}(t). \quad (8)$$

Using (5) and similarly for \tilde{s}_m in (8) for a single time step, leads to

$$\frac{d}{dt} \tilde{P}_m(t) = g_{k+2} P_{k+2}(t) - [\tilde{g}_m + \tilde{s}_m] \tilde{P}_m(t) + s_{k-1} P_{k-1}(t). \quad (9)$$

Hence the general form [compare Eq. (1) and (6)] is restored in the reduced system of equations. Performing this joining repeatedly, finally only one state is left. This gives the same MFPT as the original ensemble of systems [4].

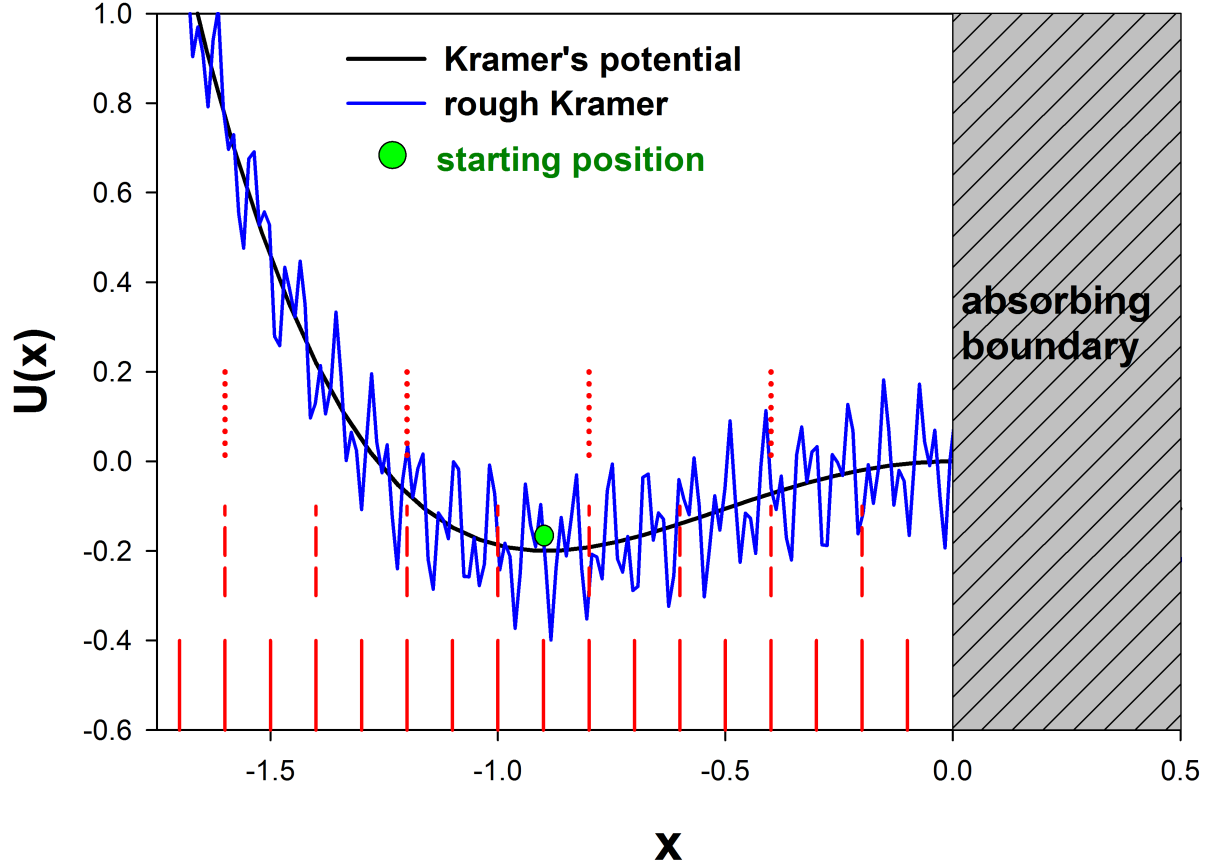


FIG. 1: (color online) Kramer's and a rough potential. The states are chosen as intervals along the x -coordinate of some fixed length Δl .

COMPUTATIONAL STUDY/SIMULATION

To illustrate the theoretical framework, we demonstrate diffusion in both dimensions $d=1$ and $d=2$, as well as the folding process of a model for a small linear polymer chain. We choose these examples to specifically address the independence of the method from any existence or knowledge of a free energy landscape or most probable escape pathway.

As a $d=1$ historical example, we studied the diffusion process of particles subjected to a Kramers or to a rough [11] potential (Fig. 1). The trajectories were integrated along 5120 individual paths starting at $x=-0.9$ and terminated once they leave the domain $(-\infty, 0]$ at the absorbing boundary $x = 0$. The MFPTs were calculated using Eq. (4). In order to show the freedom in choosing the length of the intervals, we show examples of bins with different

lengths Δl . Starting at the absorbing boundary $k=0$ for $x \geq 0$, the system resides in state k when $(k-1)\Delta l \leq x < k\Delta l$. In both cases (smooth and rough), we chose $\Delta l = 0.1, 0.2$ and 0.4 [Fig. (1)]. Table I shows the results obtained with the PD method are not changed with different interval lengths. A comparison with a direct measurement (on the underlying dynamics) and the semi-analytical solution further verifies that the MFPTs obtained with the PD method gives reliable results (provided that sufficient statistics are obtained to get accurate estimates of the growing and shrinking rates). Note that to illustrate the method we chose examples of the starting position being at the boundary between two states ($\Delta l = 0.1$), in the midrange ($\Delta l = 0.2$), and away from the midrange ($\Delta l = 0.4$) of the starting state. The results do not change with any of these starting positions, which further indicates the independence of the PD method.

As a $d=2$ example we applied the PD method to the diffusion process at the entropic barrier $U_{entr}(x, y)$ of Ref. [8]. We chose the coordinate ζ in two different ways. The trajectories are started at $(x_o, y_o) = (-0.5, 0)$ and terminated once they reach $x > 0$. We obtained results for defining the states both with the coordinate $\zeta=x$ and $\zeta=r$ [Fig. (2)]. The first represents a binning along the x-coordinate, interpreted as the progress towards the absorbing boundary, while the circular binning has no such interpretation. For $\zeta=x$ the states were $(k-1)\Delta x \leq x < k\Delta x$, where we chose $\Delta x = 0.065$ and 0.13 . For $\zeta=r$, the states are defined as $(S-k)\Delta r \leq r < (S-k+1)\Delta r$ for $2 \leq k \leq S$, where r denotes the distance from (x_o, y_o) . We chose $\Delta r = 0.025$ and 0.05 . For the circular binning, the bin $k=1$ is comprised of all points with $x \leq 0$ outside the circular annuli. The results in Table I showing independence of the MFPT illustrate the strength of the PD method.

As a polymeric example, we applied the PD method to the folding process of a model of a small linear polymer chain having the chemical structure $(HP_3)_5H$, where H stands for the hydrophobic and P for the polar monomers. The structure of the individual chain is maintained by three interatomic potentials: a bond-stretching potential, a bond-angle bending potential, and a rejecting potential avoiding an overlap of HP or PP monomers. The chain undergoes a folding process from the fully elongated state to a compact near native state caused by attractive Lennard-Jones type of interactions between HH monomers. The PD method is given by choosing the coordinate ζ as the potential energy of the native contacts (the HH interaction energy). Although this choice seems apparent, it does not correspond to an actual dynamical coordinate. Starting with the fully elongated chain, for

$k_B T$	Projective Dynamics				
	$\Delta l = 0.1$	$\Delta l = 0.2$	$\Delta l = 0.4$		<div>Brownian motion</div> <div>Riemann integration</div>
0.1^a	18.4(± 0.2)	18.4(± 0.2)	18.4(± 0.2)		18.4(± 0.2) 18.44
0.0875^a	24.7(± 0.3)	24.7(± 0.3)	24.7(± 0.3)		24.7(± 0.3) 24.80
0.075^a	36.3(± 0.4)	36.3(± 0.4)	36.3(± 0.4)		36.3(± 0.5) 36.46
0.0625^a	62(± 1)	62(± 1)	62(± 1)		62(± 1) 61.9
0.1^b	46.3(± 0.6)	46.3(± 0.6)	46.3(± 0.6)		46.3(± 0.6) 46.2
0.0875^b	80(± 1)	80(± 1)	80(± 1)		80(± 1) 81
0.075^b	179(± 1)	179(± 1)	179(± 1)		178(± 2) 178
	$\Delta r = 0.025$	$\Delta r = 0.05$	$\Delta x = 0.065$	$\Delta x = 0.13$	
0.1^c	15.0(± 0.1)	15.0(± 0.1)	15.0(± 0.1)	15.0(± 0.1)	15.0(± 0.2)
0.0875^c	17.3(± 0.2)	17.3(± 0.2)	17.3(± 0.2)	17.3(± 0.2)	17.3(± 0.2)
0.075^c	20.8(± 0.3)	20.8(± 0.3)	20.8(± 0.3)	20.8(± 0.3)	20.8(± 0.3)
0.0625^c	24.2(± 0.1)	24.2(± 0.1)	24.2(± 0.1)	24.2(± 0.1)	24.2(± 0.3)
0.05^c	30.3(± 0.5)	30.3(± 0.5)	30.3(± 0.5)	30.3(± 0.5)	30.3(± 0.4)
	$\Delta U/C_h \approx 1$	$\Delta U/C_h \approx 2$			
2.75^d	9.31(± 0.03)	9.31(± 0.03)			9.31(± 0.02)
2.50^d	9.99(± 0.03)	9.98(± 0.03)			9.99(± 0.02)
2.25^d	10.92(± 0.03)	10.90(± 0.03)			10.92(± 0.02)
2.00^d	12.58(± 0.04)	12.56(± 0.04)			12.58(± 0.02)
1.75^d	15.34(± 0.05)	15.31(± 0.05)			15.34(± 0.04)

TABLE I: MFPTs for (a) Kramer’s potential, (b) rough 1 dim. (c) 2-dim. entropic barrier and (d) the folding of a polymer chain. The results of the Projective Dynamics method are given for their corresponding intervals $\Delta\zeta = \Delta l$ Kramer’s, Δr and Δx 2-dim, and $\Delta U/C_h$ polymer. Also shown results obtained by direct measurement of the Brownian motion process and the semianalytical solution for the $d=1$ absorption processes.

different temperatures of the external bath, we simulated the folding process due to the Brownian motion. We compared the MFPTs of the chain of reaching a potential energy deep enough in the basin of attraction of the energy ground state (i.e. the native state) so that no escape (i.e. unfolding) from there is likely to occur. The results of the PD method

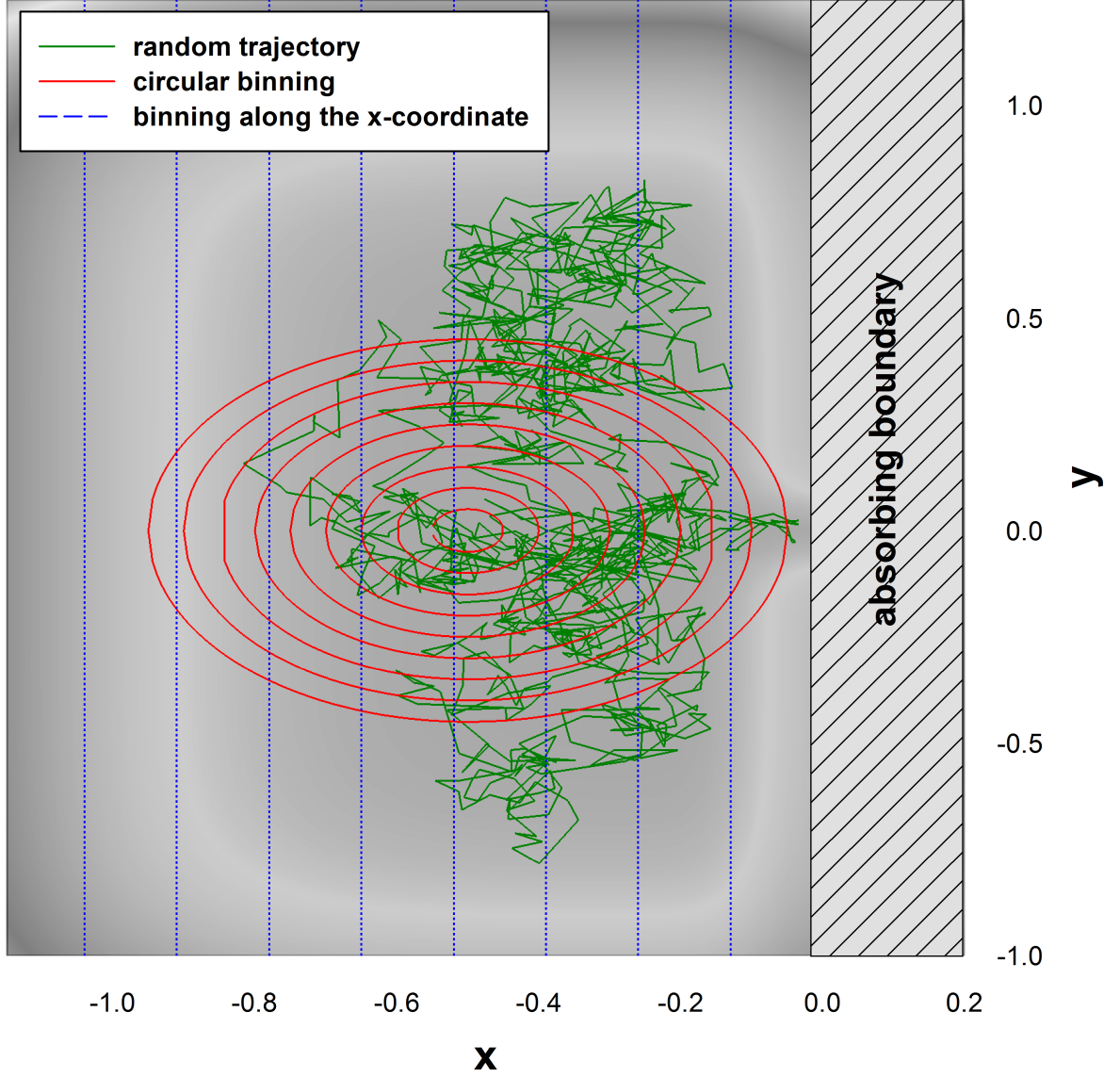


FIG. 2: (color online) The entropic barrier, the states are defined along the coordinate $\zeta = x$ (representing a progress toward the absorbing boundary) and $\zeta = r$ (representing circular intervals) of some fixed interval length $\Delta\zeta = \Delta x$ and Δr .

as well as a direct measurement are shown in Table I. For all simulated temperatures the PD method gives the same results (within statistics) as a direct measurement.

CONCLUSION AND DISCUSSION

The Projective Dynamics (PD) method, as a tool for projecting multi-dimensional systems onto one set of states $\{\zeta_k\}$ and mapping the time-evolution onto a discrete master equation with nearest neighbor coupling, was shown to be independent of the choice in the states ζ_k and the ‘length’ of the intervals which define the states. Provided only transitions between adjacent states occur, the PD method correctly obtains MFPTs. This result makes the PD method generally applicable to the dynamics of any system (discrete or continuous, Markovian or non-Markovian, stochastic or deterministic). Subject only to the nearest-neighbor coupling constraint, the states $\{\zeta_k\}$ can be chosen in multiple ways, without changing the mean first-passage time (MFPT). In many cases of interest, the average occupation probability for every state ζ_k is also the same as for the original dynamical system. The calculation of the growing and shrinking rates required in the PD method may for some models and dynamics be obtained by using other methods, such as calculations of histories [12] or forward flux sampling [13] or accelerated molecular dynamics [14, 15].

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